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# Gas Sensors- A Review

**S. Karthikeyan[1]*, Haresh M. Pandya[2], M. U. Sharma[3], K. Gopal[4]**

[1] *Department of Chemistry, Chikkanna Government Arts College, Tiruppur, TN, India.
[2]Department of Physics, Chikkanna Government Arts College, Tiruppur, TN, India.
[3]Defence Scientist (DRDO), Solid State Physics Laboratory, New Delhi, India.
[4]Department of Chemistry, Erode Arts & Science College, Erode, TN, India.

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## Abstract

*Chemical sensors for specific species with varying sensitivity levels are commercially available. Common chemical sensors defer in terms of the sensing material and the nature of property change such as electrical conductivity, optical characteristics and temperature. Some of the current sensor technologies include high temperature oxide thin-film sensors, polymer based sensors, catalytic based sensors and surface acoustic wave* (SAW) *sensors are described. In this the sensor array consists of Carbon Nano Tube (CNT) as sensing material and an interdigitated electrode as a transducer is described. The gas sensors fabricated by using conducting polymers such as polyaniline, polypyrrole as the active layers have been reviewed. The macroscopic coaxial carbon cylinders consisting of aligned CNT stacks have been used in CNT- polymer composite. The advantages and disadvantages of each sensor technology are also highlighted. All these technologies have been used for the development of highly sensitive and responsive gas sensors for the detection of flammable and hazardous gases. However, for improved sensitivity and selectivity for these sensors, future trends and outlook for researchers are suggested in this review.*

***Keywords:*** *CNT; Combustible gas; Gas sensor; Sensitivity; SAW.*

## 1. INTRODUCTION

The air surrounding us contains different amount of gases which could be hazardous to human health, atmospheric pollutants or of significance to an industrial or medical process, It becomes therefore very imperative to detect the presence of these gases since the environment we dwell in consists of humans, plants and animals as its main inhabitants, so the safety of their lives is of topmost priority. Gas sensors are chemical sensors that are of paramount importance. A chemical sensor comprises of a transducer and an active layer for converting the chemical information into another form of electronic signal like frequency change, current change or voltage change for many centuries, different gas sensor technologies have been used for different gases detection including semiconductor gas sensors, catalytic gas sensors, electrochemical gas sensors, optical gas sensors and acoustic gas sensors. The performance characteristic of every sensor is based on some properties including sensitivity, selectivity, detection limit, response time and recovery time. Other factors that makes a sensor more attractive to consumers include small size, low power consumption and capability of being wireless.

## 2. DIFFERENT TYPES OF GAS SENSORS

### 2.1 Catalytic Sensor

The first catalytic combustion type sensor was discovered by Jonson in 1923 (Firth *et al*. 1973; Jones, 1987) and was used for the detection of methane in mines. This type of sensors usually contains a catalytic surface coated on a hot plate with Pt resistor that heats up the catalyst to a very high temperature at which any flammable gas molecules can ignite. The concentrations of gases can be detected by monitoring resistance change of the platinum resistance arising from increase in temperature. This design was recently developed by Li and Lie Xu *et al*. (2012) in which they design and fabricate a two-beam microplate for catalytic gas sensors.

#### *2.1.1 Pellistors-type catalytic gas sensor*

The term pellistor is the combination of 'pellet' and 'resister'. The sensing elements consist of small pellets of catalyst loaded ceramic whose resistance changes in the presence of the target gas. A Pellistors-type catalytic gas sensor consists of two platinum coils which serve as heater as well as resistance thermometer. It also consists of active and inactive beads. The active bead is activated with catalyst made from a metal like platinum or palladium. The inactive bead has no catalyst but usually acts as compensating elements. A voltage supply use for powering the circuit heats up the coils so that the beads are raised to a high temperature from a range of 300 °C to 500 °C depending on the target gas. This causes the gas to ignite and raises the temperature of the detector coil as shown in Fig. 1.

***S. Karthikeyan** **Tel. no:+919442264501**
**Email:** environkarthi@gmail.com

**Table 1. Types of gas sensors**

| S.No | Sensor Type | Advantages | Disadvantages |
|---|---|---|---|
| 1 | Catalytic | Simple, measures flammability of gases and low cost technology | Requires air or oxygen to work. can be poisoned by lead, chlorine and silicones |
| 2 | Thermal | Robust but simple construction. Easy to operate in absence of oxygen. Measuring range is very wide. | Reaction due to heating wire. |
| 3 | Electro-Chemical | Measures toxic gases in relatively low concentrations. Wide range of gases can be detected | Failures modes are unrevealed unless advanced monitoring technique used. |
| 4 | Optical | Easy to operate in absence of oxygen. Not affected by electromagnetic interference. Monitoring area is very wide. | Affected by ambient light interference. |
| 5 | Infrared | Uses only physical technique. No unseen failure modes. Can be used in inert atmospheres. | Not all gases have IR absorption. Sequential monitoring is slower on multi point analyzers and also more user expertise required. |
| 6 | Semi-Conductors | Mechanically robust, works well at constant high humidity condition. | Susceptible to contaminants and changes due to environmental conditions. Non-linear response effects complexity. |
| 7 | Surface Acoustic Wave | Detect nerve and blister agents Battery-less and could be used for wireless applications. Could be placed in harsh and rotating parts | Due to its small size there is difficulty in handling during fabrication process. |

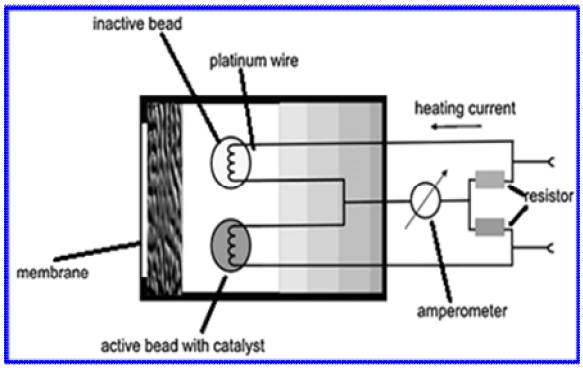


**Fig. 1: Pellistor-type gas sensor (Hubert *et al.* 2011)**

This rise in temperature increases the coil resistance and causes an imbalance in the voltage of the Wheatstone bridge which constitutes the sensor signal. These sensors are always manufactured in pairs, the active catalyzed element being supplied with an electrically matched element which contains no catalyst and is treated to ensure that no gas will oxidize on its surface. This "compensator" element is used as a reference resistance to which the sensor's signal is compared to remove the effects of environmental factors other than the presence of a flammable gas. The pellistors are capable of detecting various combustible vapours and flammable gases at concentration as low as 500 ppm with relatively fast response times.

A Review was made by Hubert *et al.* (2011) on Hydrogen gas sensors. Recent researches as reported by Lei Xu *et al.* (2010) developed catalytic combustion type methane detection sensor with a Pd-Pt catalyst working on pulse voltage mode. Eui-Bok *et al.* (2011) recently developed an integrated catalytic combustion $H_2$ sensor using MEMS technology.

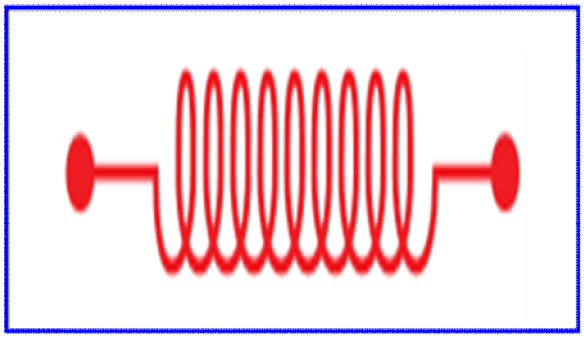

**Fig. 1(a): Hot Wire Sensor (Xu *et al.* 2010)**

The major advantages of catalytic detectors:

- Simple to operate.
- Easy to install, calibrate and use.
- Long life with a low replacement cost.
- Proven technology with exceptional reliability and predictability.
- Easily calibrated individually to gases such as hydrogen which cannot be detected using infrared absorption.
- Can perform more reliably in dusty & dirty atmospheres as they are not as sensitive as optics to the buildup of industrial contaminants.
- Can perform more reliably in high temperature applications.

- Are less sensitive to humidity and condensation.
- Not as significantly affected by changes in pressure.
- Can detect most combustible hydrocarbons.

The limiting factors in catalytic detector technology:

- Catalysts can become poisoned or inactive due to contamination (Chlorinated & Silicone compounds, prolonged exposure to $H_2S$ and other sulfur or corrosive compounds).
- The only means of identifying detector sensitivity loss is by checking with the appropriate gas on a routine basis and recalibrating as required.
- Requires oxgen for detection.
- Prolonged exposure to high concentrations of combustible gas may degrade sensor performance.
- If flooded with a very high gas concentration, may show low or no response, and sensor may be damaged or rendered inoperable.

### *2.1.2 Thermoelectric gas sensor*

The earliest thermoelectric gas sensor was developed by McAleer (1985) for the detection of combustible gas like hydrogen gas as reported by (Shin *et al.* 2003; 2004). Hydrogen detection using thermoelectric sensor is possible by producing an electrical signal based on the catalyzed exothermic oxidation reaction of hydrogen. Thermoelectric gas sensors work on the principle of the Seebeck effect. The Seebeck effect occurs as a result of a temperature difference between two points of a conductor or semiconductor material which gives rise to a voltage difference between these points.

Seung-Il Yoon *et al.* (2009) designed and fabricated a thermoelectric gas sensor based on the principle of gas adsorption instead of gas absorption. The sensor uses an embedded tin oxide catalyst for the detection of hydrogen and $NO_x$ gases. A thermoelectric gas sensor for the detection of volatile organic compounds was designed and developed by Anuradha *et al.* (2006) in which chromium metal films were deposited on the glass substrate. Sensors with chromium metal showed good sensitivity to acetone as low as 28 ppm and was found to be selective towards acetone gas and the temperature range of about 80 °C to 160 °C.

## 2.2 Thermal conductivity gas sensors

Thermal conductivity measurements for gas analysis have been used for many decades (Hubert *et al.* 2011). It is usually used for the detection of gases with high thermal conductivities greater than air like hydrogen and methane while gases with conductivities close to air cannot be detected like ammonia and carbon monoxide. Gases with thermal conductivities less than air are difficult to detect using this method due to interference. (e.g.) $CO_2$ and $C_4H_{10}$. The first type of thermal conductivity gas sensor is called pellistor like sensor. And consists of two inert resistor beads with an implanted thermo resistor. The heating element is a resistor which is located in the middle of the membrane. A gas chamber is located for the hydrogen sensing Fig. 2.

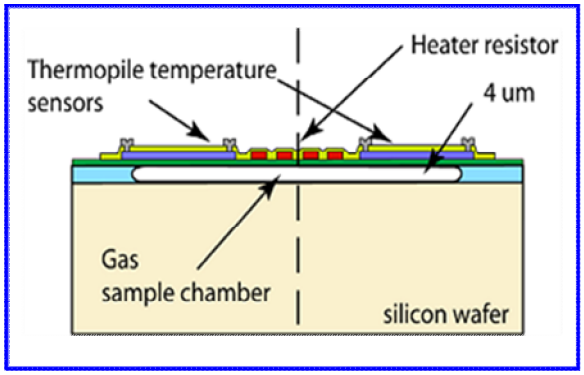


**Fig. 2: Micro-thermal conductivity gas sensor (De Graaf and Wolffenbuttel, 2012)**

Pascal Tardy *et al.* (2004) developed a dynamic thermal conductivity sensor based on the transient response of a SiC micro plate for the determination of carbon monoxide content in hydrogen and methane. Isolde Simon and Michael Arndt (2002) designed a simple micromachined thermal conductivity sensor. De Graaf and Wolffenbuttel (2012) recently developed a thermal conductivity gas sensing which uses MEMS technology for the fabrication of high sensitivity thermal sensors for hydrogen detection. The sensitivity for hydrogen in air was found to be 60 µV per % $H_2$ at 1 mW heater dissipation.

## 2.3 Electrochemical Gas Sensor

A typical electrochemical gas sensor consists of a sensing electrode or working electrode and a counter electrode which are separated by a thin layer of electrolyte. The operating principles of electrochemical gas sensors are the same as liquid electrolytic fuel cells. They are based on the electrochemical oxidation or reduction of the analytic gas at a catalytic electrode surface. Basically they detect gases by producing a chemical reaction between the gas and oxygen contained in the sensor. The reaction produces a small current which is proportional to the concentration of the gas present. These types of sensors allow gases to diffuse through a porous membrane to an electrode where it is either reduced or oxidized at the electrode. Electrochemical sensors operate by reacting with a target gas and producing an electrical signal that is proportional to the gas concentration.

Currie *et al.* (1999) developed micromachined thin solid state electrochemical sensor for simultaneous detection of $CO_2$, $NO_2$ and $SO_2$ gas. Similarly, R. Sathiyamoorthi *et al.* (2004) developed an electrochemical sensor for the detection of fluorine and chlorine. Tian Gan and Shengshui Hu (2011) published a review paper on electrochemical sensors based on graphene materials.

Typical Toxic gas electrochemical sensor specification is given below,

**Sensors type** : 2 or 3 electrodes; mostly 3 electrodes
**Range** : 2-10 times permissible exposure limit
**Life expect** : 12 to 24 months normal; depends on manufacturer and sensor
**Temp. range** : -40 $^{o}$C to +45 $^{o}$C
**Relative humidity** : 15-95% non-condensing
**Response time T80** : < 50 s.
**Long term drift** : drift down 2% per month

The following factors are the disadvantages for this type of sensor,

- While this technology is somewhat specific, other common gases will react at different levels and be detected, resulting in false positives and false alarms.
- These sensors have a limited lifetime and deplete over a period of time.
- The depletion rate is primarily determined by the sensor's exposure to the reactant gases.
- Deciding when to recalibrate these sensors to maintain a specific accuracy can be a problem.
- On average, most equipment manufacturers using electrochemical sensors recommend recalibration every three months, but this is influenced by the sensor's reactant gas exposure and the required accuracy level. Electrochemical sensors will also degrade when exposed to high humidity conditions.

### *2.3.1 Amperometric gas sensor*

The Amperometric sensors work at a constant applied voltage and the sensor signal is a diffusion limited current. It usually consists of two electrodes, the working electrode and the counter electrode and also a reference electrode which are immersed in the electrolyte solution and a potentiostat for maintaining constant voltage shown in Fig. 3. (RTILs– Room temperature Ionic Liquids). Amperometric sensors have been used for detecting various gases by changing the type of electrolyte.

Kuo-Chuan Ho and Wen- Tung Hung (2001) developed an amperometric $NO_2$ gas sensor based on Pt/Nafion electrode, $NO_2$ concentrations in the range of 0 to 485 ppm were detected. Similarly an amperometric hydrogen sensor was developed based on polymer electrolyte membrane with Nafion membrane as the conducting polymer. The response to hydrogen concentration was in the range of 260 to 11,500 ppm Yente Chao *et al*. (2005) developed an amperometric sensor using 3 different sensor designs for hydrogen and carbon monoxide sensing.

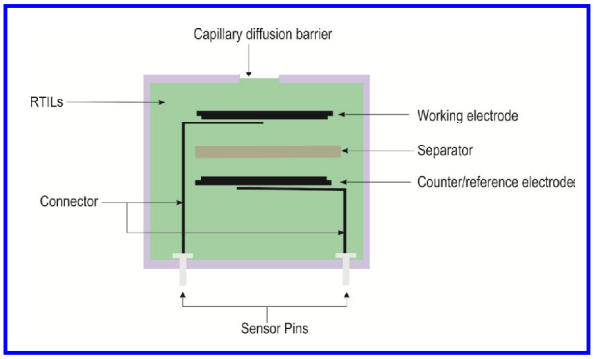


**Fig. 3: Proposed membrane-free gas detector**

An amperometric gas sensor for the detection of hydrocarbon was reported by Dutta *et al.* (2005) for monitoring in exhaust pipes. Microamperometric sensors dated back in the 1980's consisted only of microfabricated electrodes on a suitable substrate, the earliest microamperometric sensor was developed by Sleszynski and Osteryoung (1984). Recently, techniques on how to improve the sensitivity of the sensors were reported by (La *et al.* 2011; Lee *et al.* 2001).

### *2.3.2 Potentiometric gas sensor*

Potentiometric gas sensors are used to determine the analytical concentration of some components of the analyte gas. They can measure the electrical potential of an electrode without current flow. Potentiometric sensors have been used for oxygen detection. These sensors usually operate between 600 °C and 1000 °C. The electrodes are usually made from Palladium, Platinum, gold or silver. The oxygen chemical potential of the reference electrode can be fixed by known oxygen partial pressure (Gaseous reference electrode) or by a mixture of the transition metal and its oxide (Solid reference electrode) (Radhakrishnan *et al.* 2005). A typical oxygen potentiometric sensor consists of an oxygen ion conducting solid electrolyte and two electrodes deposited on the two sides of the electrolyte (Fig. 4) (Radhakrishnan *et al.* 2005).

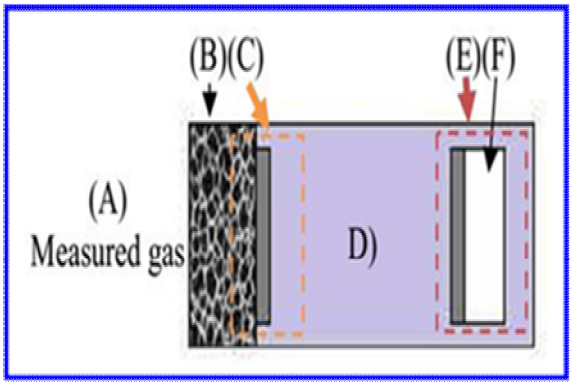


**Fig. 4: Schematic structure of a potentiometric planar oxygen Lambda sensor (Radhakrishnan *et al.* 2005)**

Where, (A) - measured atmosphere, (B) - porous protective layer (it is optional), (C) - sensing electrode,

(D) - $O_2$-ion-conductive ceramic electrolyte, (E) - reference electrode exposed to (F) ambient air atmosphere.

Lee *et al.* (2001) developed a potentiometric $CO_2$ gas sensor using lithium phosphorus oxynitride electrolyte while recently Jiun-Chan Yang *et al.* (2010) developed a high temperature $NO_2$ sensor fabricated with asymmetric reference and sensing electrode made with Pt and YSZ electrolyte. Yongtie Yan *et al.* (1995) developed a potentiometric sensor using stabilized zirconia for chlorine gas by combining MgO-stabilized zirconia tube with an auxiliary phase containing metal chloride with a sensitivity of 1-100 ppm of chlorine at 550-600 °C. Radhakrishnan *et al.* (2005) fabricated a miniaturized series connected potentiometric sensor on a silicon fabricated electrodes on after using micro fabrication techniques for oxygen detection.

### 2.4 Optical Gas Sensor

This type of sensors uses optical absorption/emission scattering of a gas species at defined optical wavelengths. An optical gas sensor consists of a light emitting element, a photo detecting element, a gas sensing element, the gas sensing element responding to light. One of the most common optical gas sensors is infrared gas sensors.

The first optical hydrogen gas sensor was reported by Butler in 1984 which consists of an optical fiber with Palladium and Titanium coatings. Crawford Massie *et al.* (2006) also designed a low-cost portable optical sensor for methane detection with very good sensitivity.

Acquaroli *et al.* (2010) designed an optical porous silicon gas sensor. Manap *et al.* (2009) developed an optical fiber sensor for the monitoring of ammonia gas using an open optical path techniques. Cross sensitivity of $CO_2$ and $O_2$ was also tested to see their effect on ammonia gas. Okazaki *et al.* (2003) also developed a fiber optic hydrogen gas sensor using catalyst-supported tungsten trioxide ($wo_3$).

The sensor used platinic acid at 500 °C and showed good response towards hydrogen gas detection and can detect gas even at room temperature. Inaba *et al.* (1979) suggested the use of a dual-wavelength laser to realize a differential absorption method that could be used over many kilometers of low-loss optical fibre, provided that suitable gas absorption bands are present. This typically involves the comparison of the received power at two, or more, different wavelengths, each having passed through a remote measurement gas cell, so that the differential absorption of the gas sample could be used to infer the concentration of the target gas. Systems that developed this principle will be discussed (Kobayashi *et al.* 1981; Hordvik *et al.* 1983; Stueflotten *et al.* 1986). A schematic of the system developed by Hordvik *et al.* (1983) is shown in Fig. 5.

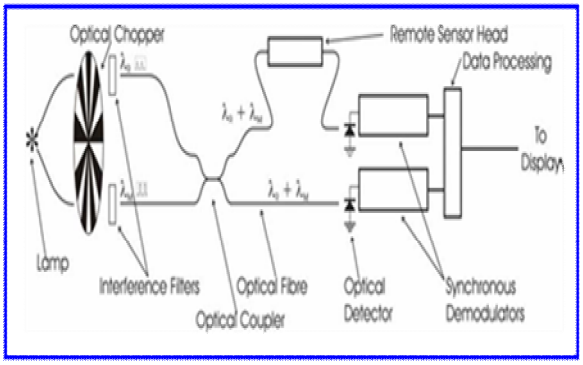


**Fig. 5: Schematic of a differential fibre-optic detection system (Redrawn from diagram in Hordvik *et al.* 1983)**

### 2.5 Infrared Gas Sensor

IR gas detection is a well-developed measurement technology. Infrared gas analyzers have a reputation for being complicated, cumbersome and expensive. However, recent technical advancements, including the availability of powerful amplifiers and associated electronic components, have opened a new frontier for infrared gas analysis. Infrared sensor consists of a detector which converts electromagnetic radiation energy into electrical signals. The Detectors are of different types namely: Thermoelectric, Thermistor Bolometer, Pyroelectric detector and Photon detector. Infrared gas sensors are use for detecting different gases like methane, ethane, propane, butane, benzene toluene, xylene and other alcohols like methanol, ethanol, etc. There are two types of optical structure which is used for the construction of infrared $CO_2$ gas sensors namely: time-double beam and space-double beams. The time-double beam optical structure has only one infrared beam emitted from the infrared source and the detector receives 2 infrared beams with different wavelengths and at different times while the space double beam structure has one infrared beam emitted from the infrared source and simultaneously enters two parallel plate detectors In this design, the space double beam is used so as to enhance the construction and a cone-shaped air chamber is designed As shown in Fig. 6.

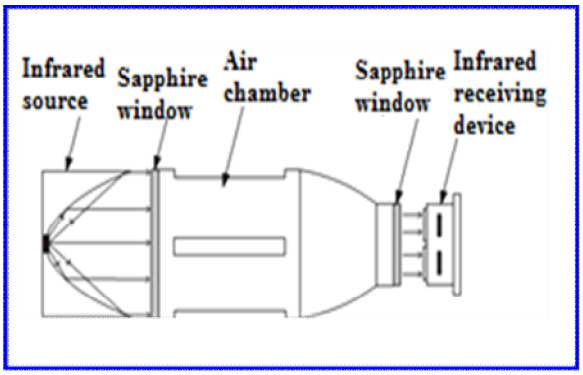


**Fig. 6: Showing a structural optical probe (Okajima *et al.* 2006).**

Okajima *et al*. (2006) developed an Infrared gas sensor using LED for the measurement of methane, absorption of gas samples between 0-97% were successfully measured, Garcia Romeo *et al*. (2012) developed a Non-Dispersive Infrared (NDIR) gas sensor for the measurement of $CO_2$ gas concentration Dong Chen *et al.* (2006) designed a tunable diode laser absorption spectroscopy for the measurement of hydrogen sulfide gas. In order to produce a sensor that is miniaturized, Guangjun Zhang *et al*. (2010) developed a miniaturized $CO_2$ sensor based on infrared absorption.

The sensor showed an accuracy of 0.026% with $CO_2$ gas concentration in the range of 0-3%. Naoya Kasai *et al*. (2011) investigated the ability of a system using a carbon infrared emitter and an Infrared camera to detect combustible gas propane.

The major advantages of IR gas detectors:

- Immunity to contamination and poisoning.
- Consumables (source and detector) tend to outlast catalytic sensors.
- Can be calibrated less often than a catalytic detector.
- Ability to operate in the absence of oxygen or in enriched oxygen.
- Ability to operate in continuous presence of gas.
- Can perform more reliably in varying flow conditions.
- Even when flooded with gas, will continue to show high reading and sensor will not be damaged.
- Able to detect at levels above 100% LEL.

The limiting factors in IR technology:

- The initial higher cost per point. IR detectors typically are more expensive than catalytic detectors at initial purchase.
- Higher spare parts cost.
- Gases that do not absorb IR energy (such as hydrogen) are not detectable.
- High humidity, dusty and/or corrosive field environments can increase IR detector maintenance costs.
- Temperature range for detector use is limited compared to catalytic detectors.
- May not perform well where multiple gases are present.

**2.6 Semiconductor Sensor**

They work on the principle of reversible gas adsorption process at the surface of the heated oxide usually oxides of tin deposited on a silicon slice by chemical vapor deposition method. A metal oxide semiconductor sensor is also known as taguchi sensor. The most widely used material is $SnO_2$ doped with small amounts of catalytic additives such as Pd or pt. The operating temperature for metal oxide semi conductor gas sensor is between 200 °C and 500 °C.

The heater at the base is used for heating up the sensor to a constant temperature of about 200-250 °C so as to speedup reaction rate. A p-type semiconductor is suitable for the detection of oxidizing gases. The oxides usually used for the n-type are mainly oxides: $SnO_2$.ZnO In $2O_3$ or $WO_3$. They are commonly used to detect hydrogen, oxygen, alcohol and harmful gases like carbon monoxide. Gas sensors using metal oxide semiconductor were first proposed by Seiyama and Taguchi (1962). However, improved sensitivity could also be obtained by the addition of doping agent in thick film semiconductor gas sensor developed for the sensing of methane and butane.

Jin Huang and Qing Wan (2009) published a review paper on the progress in gas sensors based on semiconducting metal oxide one dimensional (1D) nanostructures.

The semiconductor gas sensors have different conFigurations, one-electrode and two electrode conFiguration. Absorptions of the sample gas on the oxide surface followed by catalytic oxidation results in a change of electrical resistance of the oxide material which is then related to the sample gas concentration which is monitored by the meter as shown in Fig. 7.

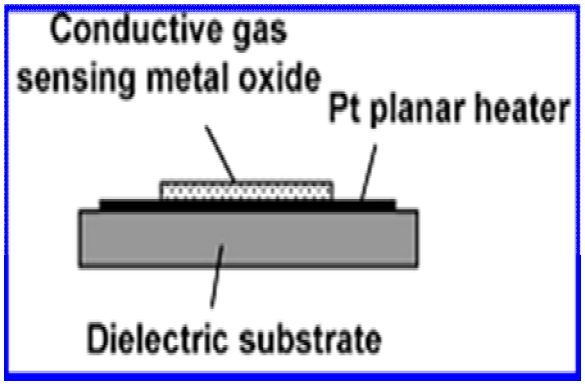


**Fig. 7: Showing one electrode configuration of semiconductor gas sensor (Zhang *et al.* 2010)**

Khodadadi *et al*. (2001) reported on improving the sensitivities of methane and carbon monoxide gases by adding 5% of $K_2O$ into $SnO_2$ samples, the sensitivity was improved by 40%. Similarly, 5% of $Na_2O$ in $SnO_2$ layers showed reduction of sensor sensitivity to CO. Addition of platinum into the prepared samples improves them response to methane. While addition of small amount of cerium oxide showed suppression of the sensor response to methane while maintaining sensitivity to CO.

The limiting factors are given below,

- MOS sensors will detect gases at lower ppm levels than electrochemical sensors.
- These sensors are less gas specific than electrochemical sensors and react with many types of gases, producing many more false positives and

false alarms. This can shut down equipment and, when used to measure toxic gases, can cause needless evacuation of personnel.

- MOS sensors are also extremely sensitive to humidity, which can affect the monitor's performance.

### 2.7 Acoustic Wave Gas Sensor

Acoustic wave sensors are so named because their detection mechanism is a mechanical, or acoustic, wave. The first acoustic gas sensor was discovered by King (1964) and was based on the measurement of bulk acoustic waves (BAW) in a piezoelectric quartz crystal resonator which is sensitive to mass changes. As the acoustic wave propagates through or on the surface of the material, any changes to the characteristics of the propagation path affect the velocity and/or amplitude of the wave. Changes in velocity can be monitored by measuring the frequency or phase characteristics of the sensor and can then be correlated to the corresponding physical quantity being measured. An acoustic wave sensor contains a receptor which is an element that is sensitive to an analyte and a transducer i.e. an element that converts the response into an electrical signal.

After intensive research studies in mid 1960's, chemical sensors for industrial atmospheric pollutants were developed. Since piezoelectric quartz resonators were used, these types of sensors were called quartz microbalances (QMB). There are different types of acoustic wave sensors which are based on the type of wave propagation.

Acoustic wave sensors have a variety of applications as in temperature, pressure, mass, chemical etc. acoustic wave sensors already possess this inherent characteristic and were used in gas sensors since 1964 so this makes it to be an attractive candidate over its gas sensing counterparts. A review on acoustic waves will be made in this section of the paper with emphasis on surface acoustic wave sensors. Another advantage of surface acoustic wave technology is that the gas sensing can be made wirelessly as shown by (Lim *et al*. 2011), which makes real online monitoring of the gas sensor. High selectivity and sensitivity have also been reported in many SAW gas sensing applications (Dutta *et al.* 2005; Yang and Dutta, 2010; Radhakrishnan *et al*. 2005).

#### *2.7.1 Surface acoustic wave gas sensor*

SAW sensors are developed based on Rayleigh waves. Surface acoustic wave sensors works based on the principle of transduction whereby the sensor converts an input electrical signal into a mechanical wave and reconverts back into electrical signal. The IDTs are made of electrodes made from either gold, aluminum or platinum. The principle of gas sensing in SAW is realized by the application of a sensing material like a thin polymer across the delay line which selectively absorbs the gas or gases of interest as depicted the frequency of operation of Rayleigh waves sensors is usually lies between 40-600 MHz.

A standard design for a SAW device is shown in Fig. 8. A transmitter interdigital electrode (Interdigital transducers, IDTs) and a receptor interdigital electrode are attached onto a piezoelectric crystal. The polymer film is coated on the gap between these two electrodes. An input radio frequency voltage is applied across the transmitter IDTs, inducing deformations in the piezoelectric substrate. These deformations give rise to an acoustic wave, traversing the gap between two IDTs. When it reaches the receptor IDTs, the mechanics energy was converted back to radio Frequency voltage (Chang *et al*. 2000, Penza *et al*. 1998). The adsorption and desorption of gas on the polymer film on the gap will modulate the wave propagation characters. A phase or frequency shift will be recorded between the input and output voltages (Penza *et al*. 1998; Milella and Penza, 1998). The detect limits of above two types of devices are very low (<1 ppm).

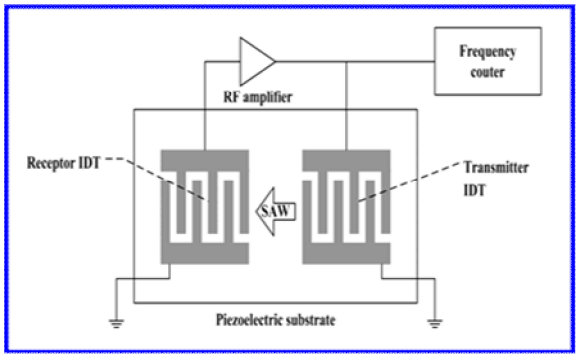


**Fig. 8: Configuration of surface acoustic wave sensor device (Chang *et al.* 2000)**

## 3. GAS SENSOR BASED ON CONDUCTING POLYMERS

Conducting polymers, such as polypyrrole, polyaniline, polythiophene and their derivatives, have been used as the active layers of gas sensors since early 1980 (Nylabder *et al*. 1983). In comparison with most of the commercially available sensors, based usually on metal oxides and operated at high temperatures, the sensors made of conducting polymers have many improved characteristics. They have high sensitivities and short response time. The conducting polymers mentioned in this review all refer (Dubbe *et al*. 2003; Zakrzewska *et al*. 2001; Timers *et al*. 2005) to intrinsic conducting polymers. Their main chains consist of alternative single and double bonds, which leads to broad $\pi$ electron conjugation. The conductivity of these pure conducting polymers are rather low ($<10^{-5}$ S cm-1).

### 3.1 The configurations and sensing principles of different sensors.

For an over view in classification of gas sensors and conFiguration of different sensors, Epic's report

(Adam *et al*. 1991) and Nylander's review (Nylabder, 1985) are two important literatures. Here, we will discuss only the widely used sensors based on conducting polymers.

### *3.1.1 Chemiresistor*

Chemiresistor consists of one or several pairs of electrodes and a layer of conducting polymer in contacting with the electrodes, as illustrated in Fig. 9. Chemiresistor are the most common type of sensors (Liu *et al*. 2004; Caravan *et al*. 2000; Ogura *et al*. 1997; Lavrik *et al*. 1996; Bearzotti *et al*. 1996; Penza *et al*. 1997; Dobay *et al*. 1999; Jin *et al*. 2003; Santhanam *et al*. 2005). They can be fabricated through a cheap and convenient process (Janata and Josowicz, 2003).

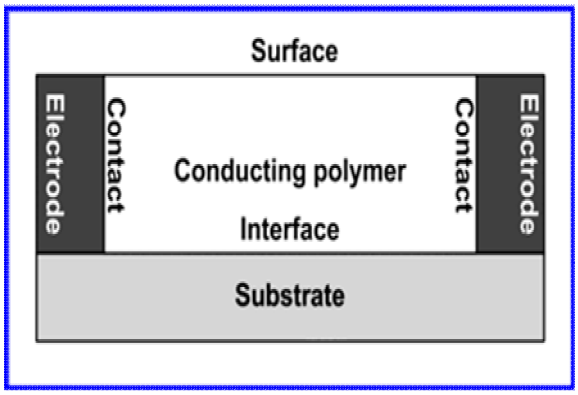


**Fig. 9: Configuration of chemiresistor**

The electrical resistance change of the sensing material is measured as the output, so a simple ohm meter is enough to collect the data. Usually, a constant current or potential is applied on the sensor, and the measuring signal is potential or current change, respectively. Alternating current (AC) also has been used as the signals of chemiresistor sensors Chemresistors are the most popular device configuration of gas sensors and many commercialized devices are based on it. The disadvantage of chemresistor is that the resistance of a device is influenced by many ambient factors and not only determined by the resistance of the conducting polymer sensing film, but also the contact resistance of the electrodes.

### *3.1.2 Transistor and Diode Sensors*

The well known Organic Thin-Film Transistors (OTFTs) have been applied in sensing field just after it was first developed (Mabeck and Malliaras, 2006). A TFT consists of a semiconductor active layer in contact with two electrodes ("source" and "drain") and a third electrode ("gate") which is separated with the active layer by an insulating film. The current flows through the other semiconducting layer, e.g. silicon. The disadvantages of these devices are, as other semiconductor devices, their preparation is slightly complicate and the characterization of a transistor is more difficult than a chemresistor.

### *3.1.3 Optic Devices*

UV-Vis and NIR spectra can reflect the electron conFigurations of conducting polymers. During the doping process, the spectral absorbance of conducting polymer film will change and new bands will appear due to the formation of polarons and bipolarons; while the spectrum can return to its original shape after dedoping (Brédas *et al*. 1984). Thus, analyte gas contacting conducting polymer film can be detected by recording the UV-vis or NIR spectral changes. An ultra thin film is suitable for fabricating an optic sensor, because the spectrum of a thin film is easy to be recorded by using commercial spectrometers. In fact, the simplest senor is just a glass covered with an ultra thin conducting polymer film. In order to online measure the spectral change with commercial UV-vis or NIR spectrometer, a special vessel is necessary. The responses of the sensors are usually the transmittance or absorbance changes of the sensing films.

## 3.2 Piezoelectric Crystal Sensor

Two types of sensors fall into this category; they are Quartz Crystal Microbalance (QCMB) and surface acoustic wave sensors. The principle and applications of piezoelectric crystal sensors are well reviewed by Chang *et al.* (2000).

### *3.2.1 Quartz Crystal Microbalance Sensor Device*

A typical schematic diagram of QCMB is shown in Fig. 10. It consists of a conducting polymer coated quartz crystal and a pair of electrodes. The resonant frequency of a quartz crystal changes with its mass load, which was described as following (Sauerbrey, 1959).

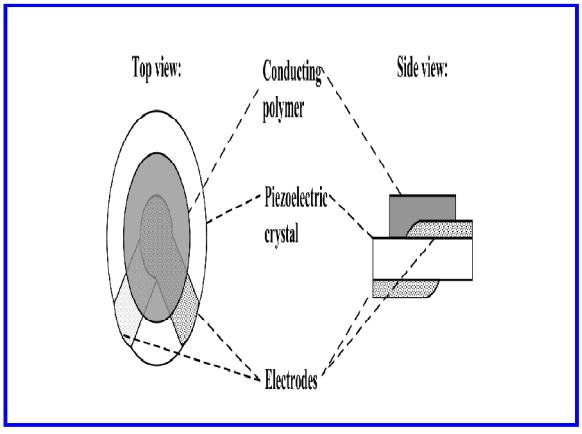


**Fig. 10: Configuration of quartz crystal microbalance sensor device**

**Table 2. Comparison of gas sensor technologies**

| Gas sensor type | Gas detected | Material Used | Temp. °C | Sensitivity | Reference |
|---|---|---|---|---|---|
| Catalytic Sensor | | | | | |
| Pellistor type Catalytic Sensor | $CH_3$ | Pt/pd | 300- 500 | - | Lei Xu *et al.*(2010) |
| Thermo-Electric Gas Sensor | H | Cu- Bi | 80- 160 | - | Mc Aleer (1985) |
| | $C_2H_5OH$, $C_6H_{14}$ | Cr | - | - | Anuradha *et al.*(2006) |
| Thermal Conductivity gas Sensor | CO in H & $CH_3$ | SiC microplate | - | - | Pascal Tardy *et al.*(2004) |
| Electrochemical Gas sensor | CO | - | - | - | Kohlraush (1885) & Haber (1900) |
| Amperometric Gas Sensor | Hydro-carbon | - | - | - | - |
| | $NO_2$ | Pt/Nafion | - | 0 to 485 ppm | Kuo chuan Ho & Wen Tung hung (2001) |
| Potentiometric Gas sensor | O | Pd, Pt, Au, Ag | 600- 000 | - | - |
| Optical Gas Sensor | H | Pd, Chromic oxide | - | - | Butler (1984) |
| Infra Red Gas Sensor | $CO_2$ ,CO, hydrocarbons | - | - | - | - |
| Semiconductor Sensor | H, O, CO, R-OH | Sn, Si | 200 - 250 | - | Seiyama and Taguchi (1962) |
| Acoustic Wave Gas Sensor | - | - | - | - | King *et al.* (1964) |
| Surface Acoustic Wave Gas Sensor | $NH_3$, CO, $CO_2$ | Al, Au, Pt | Frequency 40-60 0MHz | - | - |

**Table 3. Detect limits of sensors based on conducting polymers and their composites to several gas analytes**

| S. No | Analyte | Sensing material | Detect limit | Sensor type |
|---|---|---|---|---|
| 1 | $NH_3$ | PAni/SWNT | 50 ppb | Chemiresistor |
| 2 | $NO_2$ | PPy/PET<br>PTh/CuPc<br>PAni/In2O3 | <20 ppm<br>4.3 ppm<br><0.5 ppm | Chemiresistor<br>Chemiresistor<br>SAW |
| 3 | HCl | PAni/FeAl | 0.2 ppm | Chemiresistor |
| 4 | $H_2S$ | PAni/heavy metal salts | <10 ppm | Chemiresistor |
| 5 | CO | PAni/FeAl<br>PAni/In2O3 | 10 ppm<br><60 ppm | Chemiresistor<br>SAW |
| 6 | Water | PAni | < 25 ppm | Chemiresistor |
| 7 | Methanol | PAni/Pd | <1 ppm | Chemiresistor |
| 8 | Methane | halide Poly(3-methylthiophene)/MWNT<br>PAni/Cu | Several ppm<br><10 ppm | Chemiresistor<br>Chemiresistor |
| 9 | Acetone | PTh copolymer | 200~ 300 ppm | Chemiresistor |
| 10 | Toluene | PTh copolymer | 20 ppm | Chemiresistor |
| 11 | Butyl amine | Poly(anilineboronic acid) | 10 ppb | Chemiresistor |

## 4. CARBON NANOTUBE BASED GAS SENSOR

Besides selectivity being an issue $SnO_2$ and other metal oxide based sensors operate only at elevated temperatures typically over 200 °C was proposed by Mishra and Agarwal (1998). Adding CNTs to an otherwise non responsive polyaniline allows CO sensing in the range of 100-1000 ppm at room temperature was done by Wanna *et al.* (2006). Vertically aligned CNTs decorated with Pt, Ru and Ag cluster responded to 0.1% CO at 150 °C when exposed to a mixture of CO, $CO_2$, $NH_2$, $CH_4$ and $NO_2$ with the mixture representing a landfill gas was proposed by Penza *et al.* (2010). The nano wire form of the metal oxides has been considered in gas sensor construction in reason has by Meyyappan and Sunkara (2010). Recently $Pd/SnO_2$ sensors have been shown to have good sensitivity in the range of 6-18 ppm of CO at a temperature of 60 °C have been proposed by Kim *et al.* (2013). MWNTs with the aid of nitrogen doping also show a good response to CO in the range of 2-20 ppm at ambient and 150 °C conditions has been proposed by Adjizian *et al.* (2014). Catalytic combustion based sensors rely on oxidation of CO and measuring the change in resistance of a metal electrode. Recently novel catalysts that can oxidize at 70 °C have been proposed by Hosaya *et al.* (2014).

## 5. POLYMER CNT COMPOSITE

The formation of macroscopic carbon cylinders (diameter 0.5 cm and length 5 cm) Consisting of ordered and aligned CNTs (diameter 200-300 nm and length 100 nm) through CVD technique by spraying benzene and ferrocene as a precursor (Srivastava *et al.* 2004). This carbon cylinder was used in the filtration of heavier hydrocarbon species from petroleum and also in the removal of bacteria from the drinking water. The coaxial carbon cylinder has been characterized through scanning electron microscopy (SEM) technique.

Currently three methods are widely used to incorporate CNTs into polymers.

1. Solution mixing or film casting of suspensions of CNT s in dissolved polymer (Kymakis *et al.* 2002).
2. In situ polymerization of CNT – polymer monomer mixture (Jia *et al.* 1999).
3. Melt mechanical mixing of CNTs with polymers (Jin *et al.* 2002).

The benzene- ferrocene precursor flow with the carrier gas Ar, Fe particles get deposited on the inner walls of the quartz tube through dissociation of ferrocene further supply of precursor allows the dissociation of hydrocarbon on these precipitate Fe Particles. The precursor and Ar gas pass through the first CNTs stack and reach the base i.e. the quartz tube from where the CNT stack growth takes place. The coaxial carbon cylinders consisting of aligned CNT stacks have been prepared by controlled spray pyrolysis technique employing benzene- ferrocene (~30 mg/ml) precursor and Ar as carrier gas. The coaxial carbon cylinders consisting of aligned CNTs have been prepared without using any patterned substrates. The CNT stacks have been produced by periodically interrupting the flow of precursor. The MWNTs polymer composite films have been prepared by solution cast technique and then these have been characterized by employing the SEM technique. The conductivity measurements on the MWNTs-PEO composite films with highest concentration of MWNTs showed an increase of eight orders of magnitude in conductivity from bare PEO film. The temperature dependence of the conductivity for MWNTs–PEO composite showed predominantly semiconducting behavior.

The coaxial carbon cylinders were prepared by spray pyrolysis of benzene- ferrocene solution in Ar atmosphere at 900 °C temperature (Mishra *et al.* 2007). The CNTs polymer (E.g. polyethylene oxide, polyacrylamide) composites were prepared by solution cast technique (Awasthi *et al.* 2006). The CNTs were synthesized by the vapour phase pyrolysis of ferrocene along with ethylene (Awasthi *et al.* 2003). The ratio of CNTs in this work corresponds to 5, 10, 15, 20, 30, 40 and 50 for which films were prepared. The growth of carbon cylinder consisting of only one layer of radically aligned MWNTs has earlier been studied (Srivastava *et al.* 2004).

## 6. CONCLUSION

This review paper presents the study of different types of advanced model sensors for various gas detections and so different sensing techniques were discussed includes catalytic, electrochemical, optical, thermal and acoustic. In which SAW sensors have been relatively modest commercial success to date and the characteristics of the sensors such as sensitivity, selectivity, high response time and Fast recovery time should be analyzed.

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